

# Transient Numerical Modeling of the Combustion of Bi-Component Liquid Droplets: Methanol/Water Mixtures

A. J. Marchese and F. L. Dryer

Department of Mechanical and Aerospace Engineering  
Princeton University  
Princeton, NJ, 08544

## Introduction

An obvious limitation to any detailed combustion modeling is the comparatively short list of fuel/oxidizer systems whose chemical kinetic mechanism is understood and reasonably validated. The list shortens considerably further when adding the additional constraint inherent to many practical combustion systems that the fuel be liquid at atmospheric conditions. Consequently, to date, numerical modeling of the time-dependent, spherically symmetric combustion of a pure, single-component liquid fuel considering detailed molecular transport and complex chemical kinetics<sup>1</sup> has focused primarily on methanol ( $\text{CH}_3\text{OH}$ ), a liquid fuel whose relatively simple oxidation chemistry has been extensively studied.<sup>2</sup> Semi-empirical chemical kinetic mechanisms<sup>3</sup> have also been successfully utilized in steady state modeling of n-heptane ( $\text{C}_7\text{H}_{16}$ ) droplet combustion.<sup>4</sup> However, recent transient n-heptane droplet modeling results suggest that such mechanisms fail to accurately capture the transition from non-burning to burning states due to the lack of detailed initiation chemistry included in these mechanisms.<sup>5</sup>

In light of the above arguments, the transient numerical modeling of bi-component liquid droplets is limited further still to those mixtures for which the gas phase chemistry of both components is well-characterized. While, much interesting physical phenomena of multi-component droplet combustion has been attributed to the volatility and liquid-phase mass diffusion of each component in the liquid fuel mixture<sup>6</sup>, the transient processes of ignition and extinction cannot be properly examined unless the gas phase chemistry of each component is understood. One bi-component liquid droplet system which can, however, be readily studied numerically is the mixture of methanol/water. Although in this case both components are not fuels, the species  $\text{H}_2\text{O}$  is, obviously, already included in the detailed gas phase oxidation chemistry of Ref. 2. In addition, substantial literature exists on the liquid mixture density, vapor/liquid equilibria, and liquid diffusion coefficients for this binary mixture. Thus, microgravity experiments of methanol/water droplets and the numerical modeling described in this study will provide an additional test for the chemical kinetic mechanism and provide further insight into bi-component droplet combustion.

Accordingly, the combustion of pure methanol and methanol/water mixtures will be studied using 2 separate droplet combustion experiments which are under development at NASA to be flown aboard space-based platforms within the next several years. The Fiber Supported Droplet Combustion Experiment (FSDC) will consist of a thin fiber upon which multiple droplets of up to 5 mm in diameter will be grown and ignited in air. The Droplet Combustion Experiment (DCE) will consist of free droplets which will be grown, deployed, and ignited in  $\text{O}_2/\text{N}_2$  and  $\text{O}_2/\text{He}$  oxidizing environments. In order to refine the FSDC and DCE test programs, and analyze the subsequent results, the combustion of a single, isolated liquid bi-component droplet of methanol/water was numerically simulated using a fully time-dependent, spherically symmetric droplet combustion model recently developed at Princeton University. The results will be described below.

## Numerical Model

The fully time-dependent, spherically symmetric, single-component droplet combustion model recently developed at Princeton University and originally described in Ref. 1 was expanded for this study so that the numerical simulation of the combustion of bi-component liquid droplets is now possible. This model currently incorporates detailed multi-component molecular transport<sup>7</sup> and complex chemical kinetic mechanisms<sup>8</sup> in the gas phase, semi-empirically formulated binary vapor-liquid equilibria at the droplet surface<sup>9</sup> and considers liquid species mass transfer and the conservation of energy within the liquid droplet interior. In addition, the non-ideal temporal and spatial variation in liquid droplet density due to the variation in temperature and liquid composition within the droplet has also been included.

For this present study of binary methanol/water mixtures, the gas phase chemical kinetics were modeled using the comprehensive methanol oxidation mechanism developed by Held which considers 89 forward chemical reactions and 21 species (Ref. 2). The experimental data and correlations of H. Lee, et. al.<sup>10</sup>, Kurihara, et. al.<sup>11</sup>, and Y.E. Lee, et. al.<sup>12</sup> were utilized to describe, respectively, the liquid density

variation, liquid/vapor equilibria, and the liquid diffusion coefficients of the binary methanol/water mixture.

## Results

In order to refine the FSDC test program and analyze the subsequent results, the transient numerical droplet combustion model described above was used to model the spherically-symmetric combustion of methanol/water droplets of up to 5 mm initial diameter in air. Table 1 is a summary of these results for 1 mm (1000 micron) methanol/water droplets in air at 1 atm. As the table shows, the model predicts a 16% decrease in instantaneous gasification rate as initial water content is increased from 0 to 50 per cent. This effect is predominantly due to the increased droplet density due to the increased water content. Indeed, simulating the identical conditions but holding density constant results in only a 3% decrease in gasification rate over the same range of initial water content. Interestingly, the total burn time increased due to decrease in gasification rate between the 0% and 25% initial water content cases, but decreased as the initial water content increased from 25% to 50% due to the increase in extinction diameter.

Table 1. Numerical results for methanol/water droplet combustion: 1000 micron initial diameter, 1 atm, Air

Initial Water Content [mass %]	Gasification Rate [mm <sup>2</sup> /s]	At $t = 0.8$ s			At Extinction	
		Flame Temperature [K]	Flame Standoff [ $d_f/d_i$ ]	Total Burn Time [s]	Extinction Diameter [micron]	Water Content [mass %]
0	0.63	1810	3.37	1.61	101	19.5
25	0.58	1697	2.85	1.69	236	43.6
50	0.53	1493	2.41	1.20	624	59.8

Figure 1 shows the main gas phase species, heat release, and temperature profile surrounding 1 mm methanol/water droplets of, initially, 0, 25, and 50 per cent water at 0.8 seconds after ignition in 1 atm air. The figure shows that, while the flame temperature decreases with increasing initial water content, the flame is positioned closer to the droplet surface. The physical phenomena governing the decrease in flame stand-off is two-fold. Firstly, the increased droplet water content results in a decrease in the gas phase methanol mass fraction at the droplet surface. Thus, in order to achieve stoichiometric methanol/oxygen consumption rates at the flame, the flame front must be positioned closer to the droplet surface. Secondly, the increase in water content results in a higher latent heat of vaporization which requires an increased heat flux applied to the droplet surface.

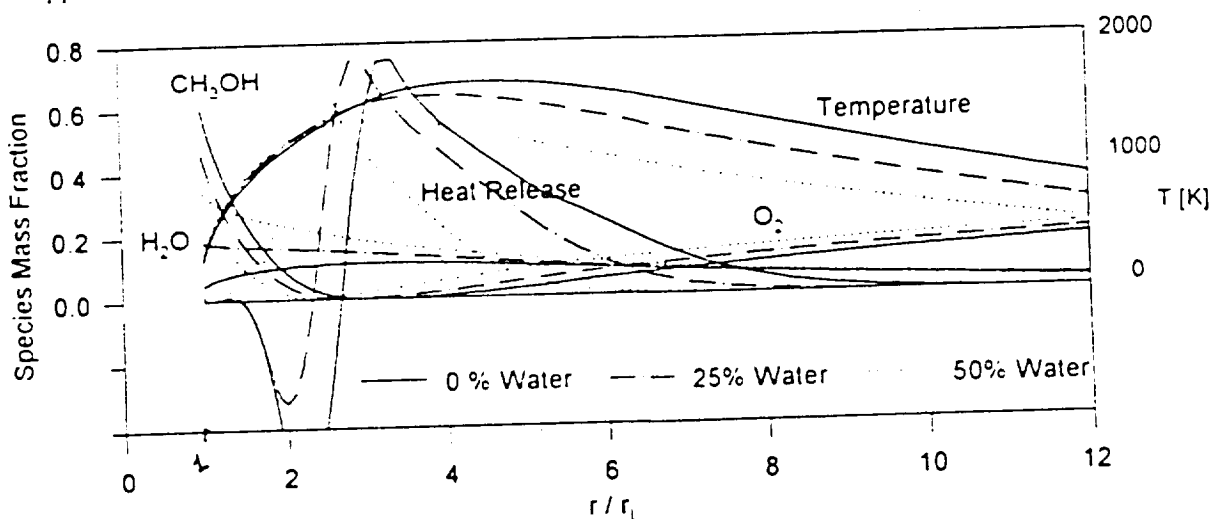


Figure 1. Gas phase species, normalized heat release, and temperature profile surrounding 1mm methanol water droplets of initially 0, 25, and 50% water in 1 atm air

Figure 2 shows the instantaneous maximum flame temperature for the above conditions. This figure suggests that the continuously varying surface liquid water mass fraction and associated surface gas phase water mass fraction coupled with the finite rate chemistry of methanol oxidation results in a continuous monotonic decrease in flame temperature for each condition. As the droplet surface regresses, the residence time in the flame decreases until flame extinction occurs resulting in the steep drop in flame

temperature. As initial water content is increased, not only does the flame temperature decrease, but the variation in flame temperature with time is more pronounced and the drop off in flame temperature at extinction is more abrupt

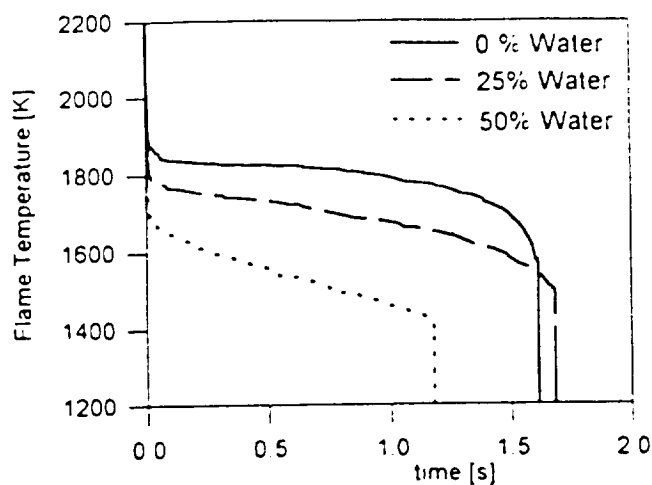


Figure 2. Instantaneous flame temperature for 1mm methanol/water droplets of initially 0, 25, and 50% water in 1 atm air

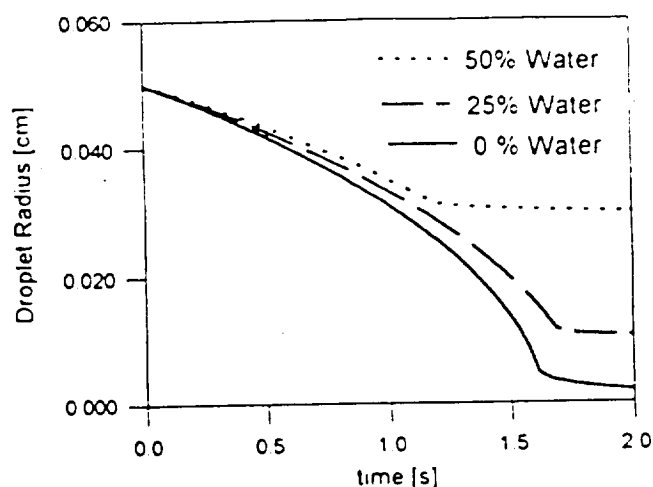


Figure 3. Instantaneous droplet radius

Figures 3 through 5 show the instantaneous droplet radius, gasification rate (instantaneous time rate of change of the square of the diameter), and average integrated droplet density. These figures clearly show that the addition of water to the methanol droplet results in decreased gasification rate primarily due to the difference in initial density of the mixture. The calculation of instantaneous average integrated droplet density (Fig. 5) showed that for each case the density variation was less than 5% during combustion, with the majority of the density variation occurring after flame extinction. As shown in Fig. 3, the radius at which the droplet extinguishes (as signified by the sharp bend in the radius vs. time curve)

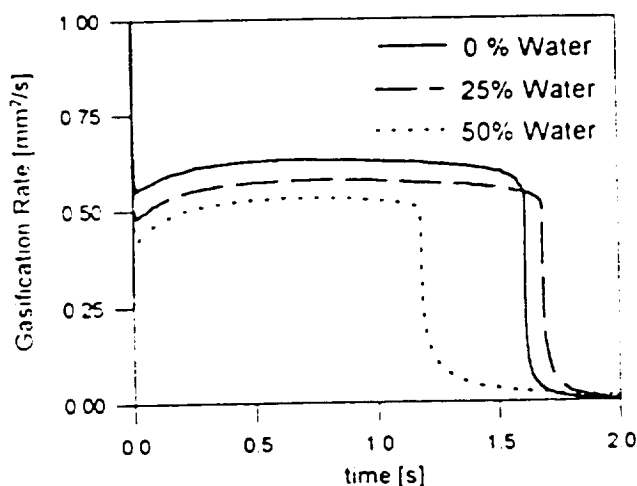


Figure 4. Instantaneous gasification rate

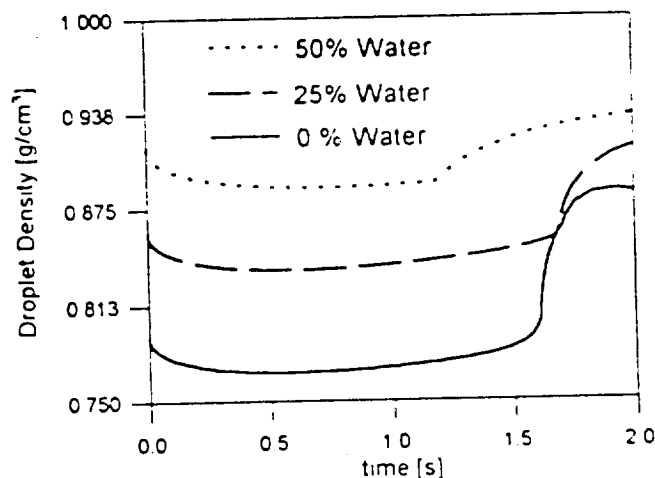


Figure 5. Instantaneous integrated droplet density

increases significantly with increasing initial water content. Experimentally, this phenomena is extremely desirable. Firstly, the overall decrease in burn time expands the envelope of test conditions which can be performed on earth using drop towers. Secondly, as is also apparent in examining Fig. 3, the dramatic increase in the diameter of the extinguished droplet results in slow post-combustion vaporization due to the dissipation of the residual enthalpy in the flame. This should result in more accurate measurements of extinction diameter.

Test results of Lee, et al. wherein falling droplets were ignited by passing through a flat flame burner have reported that, at extinction, initially pure methanol droplets contained up to 80% water.<sup>13</sup> Moreover, suspended droplet tests performed by Choi on mixtures of water/methanol in 1-g showed that

this 80% value was relatively insensitive to the initial droplet water content.<sup>14</sup> These experiments differ from the numerical modeling of the present study, however. In the former experiment, the high ambient temperatures resulted in very small extinction diameters, in the latter, natural convection due to buoyancy would have greatly enhanced the rate at which flame-generated water was delivered to the droplet surface. As shown in Fig. 6 and summarized in table 1, the total integrated water mass fraction in the liquid droplet did not approach 80% and varied with the initial water content. This is not surprising when considering the differences between the spherically-symmetric model and the experiments.

Finally, figure 7 is a plot of the fractional gasification rate of methanol. Interestingly, this plot suggests that for 1 mm droplets with initial water content slightly greater than 25%, flame-generated water will not dissolve back into the droplet (A methanol fractional gasification rate value greater than unity results when there is a net flow of water into the droplet).

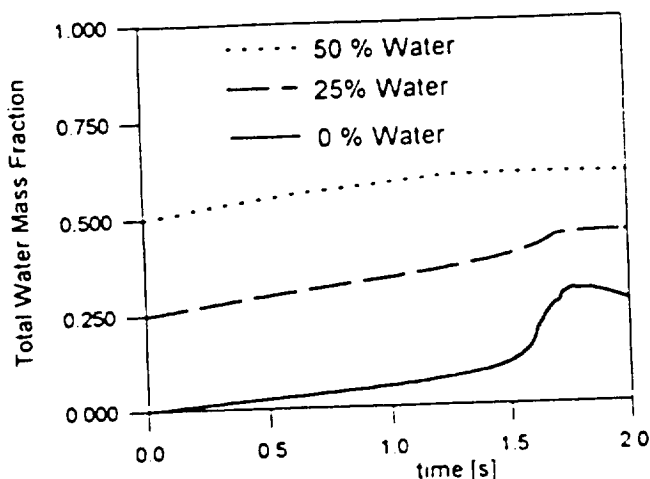


Figure 6. Total integrated liquid water mass fraction

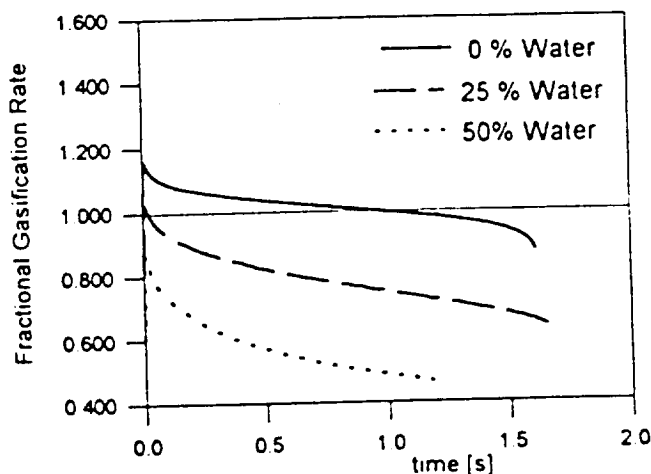


Figure 7. Fractional gasification rate of methanol

## Conclusions

This study shows that liquid mixtures of methanol and water are attractive candidates for microgravity droplet combustion experiments and associated numerical modeling. The gas phase chemistry for these droplet mixtures is conceptually simple, well understood and substantially validated. In addition, the thermodynamic and transport properties of the liquid mixture have also been well characterized. Furthermore, the results obtained in this study predict that the extinction of these droplets may be observable in ground-based drop tower experiments. Such experiments will be conducted shortly followed by space-based experiments utilizing the NASA FSDC and DCE experiments.

## Acknowledgment

The authors gratefully acknowledge the support of the National Aeronautics and Space Administration through Grant No. NAG3-1251.

## References

- <sup>1</sup>Cho, S. Y., Yetter, R. A., and Dryer, F. L., *Journal of Computational Physics*, (1992), 102, 160-179.
- <sup>2</sup>Held, T. J., PhD Thesis, Dept. of M.A.E., Princeton Univ., Princeton, NJ (1993).
- <sup>3</sup>Warnatz, J., *Twentieth Symposium (International) on Combustion*, p. 845, (1984).
- <sup>4</sup>Jackson, G. S., and Avedesian, C. T., Fall Technical Meeting ESSEI, (1993).
- <sup>5</sup>Marchese, A. J., and Dryer, F. L., Princeton University M.A.E. Report.
- <sup>6</sup>Law, C. K., and Law, H. K., *Modern Developments in Energy, Combustion, and Spectroscopy*, pp. 29-48, (1994).
- <sup>7</sup>Kee, R. J., Warnatz, J., and Miller, J. A., *Sandia Report SAND83-8209* (1983).
- <sup>8</sup>Kee, R. J., Rupley, F. M., and Miller, J. A., *Sandia Report SAND89-8009* (1989).
- <sup>9</sup>Hirata, M., Ohe, S., and Nagahama, K., *Computer-Aided Data Book of Vapor-Liquid Equilibria*, Kodansha Sci., (1975).
- <sup>10</sup>Lee, H., Hong, W., and Kim, H., *J. Chem. Eng. Data* (1990), 35, 371-374.
- <sup>11</sup>Kurihara, K., Nakamichi, M., and Kojima, K., *J. Chem. Eng. Data* (1993), 38, 446-449.
- <sup>12</sup>Lee, Y. E., and Li, F. Y., *J. Chem. Eng. Data* (1991), 36, 240-243.
- <sup>13</sup>Lee, A., and Law, C. K., *Combust. Sci. and Tech.* (1992), 86, 253-265.
- <sup>14</sup>Choi, M. Y., PhD Thesis, Dept. of M.A.E., Princeton Univ., Princeton, NJ (1992).

Don't know it!